# PATENT ABSTRACTS OF JAPAN

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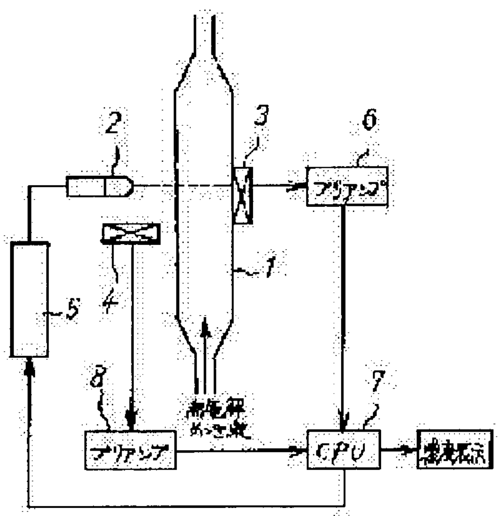
## (54) METAL ION CONCENTRATION MEASURING METHOD OF NONELECTROLYTIC PLATING SOLUTION




(57)Abstract:

PROBLEM TO BE SOLVED: To enable with high accuracy even in the case that the concentration of a plating solution is increased and that a transmittance is reduced by increasing the output of a light source and increasing the amount of projection light at the time when the transmittance is reduced in absorptiometry.

SOLUTION: Light emitted from a light source 2 is transmitted through a flow cell 1 into which a nonelectrolytic plating solution is introduced. Transmitted light is received at a photosensor 3. The output of the phtosensor 3 is amplified at a preamplifier 6 and is inputted to a CPU 7. The output of a phtosensor 4 is also amplified at a preamplifier 8 and is inputted to the CPU 7. The CPU 7 operates a transmittance from the amount of projection light and the amount of transmitted light. When the concentration of the plating solution becomes high and the transmittance operated by the CPU 7 is reduced, a signal is sent from the CPU 7 to a light source electric power controller 5 to increase the electric power supplied to the light source 2 and to increase the amount of projection light. By this, as the absolute value of amount of transmitted light is increased, errors in absorbance are not increased.

CLAIMS

[Claim(s)]

[Claim 1] The metal ion density measurement approach of the nonelectrolytic plating liquid characterized by in measuring the metal ion concentration of nonelectrolytic plating liquid with an absorptiometry heightening the output of the light source when permeability falls, and measuring by making the amount of floodlighting increase

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Field of the Invention] This invention relates to the metal ion density measurement approach of the nonelectrolytic plating liquid by the absorptiometry.

[0002] [Description of the Prior Art] The metal ion in plating liquid deposits as a metal on a work-piece front face by the catalytic reduction reaction of a work-piece metal, and along with it, metal ion concentration, reducing-agent concentration, pH, etc. fall gradually, and go by nonelectrolytic plating, such as non-electrolyzed nickel plating. Therefore, plating liquid is sampled, metal ion concentration is measured with an absorptiometry, and plating liquid management maintained at the value which was always able to define the amount of metal ions in plating liquid etc. is performed.

[0003] The metal ion density measurement by this absorptiometry leads nonelectrolytic plating liquid to the interior of a flow cell 1, as shown in drawing 3 , and it is performed by the approach of measuring the quantity of light which applied light from the light source 2 and was penetrated with photosensor 3. When the amount of floodlighting from the light source 2 is set to L0 and the amount of transmitted lights measured by photosensor 3 is set to L1, it is $t=L1 / L0$. It is called permeability and $E=\log (1/t)$ is called absorbance. In this case, since an absorbance E is generally in direct proportion to metal ion concentration, it can ask for the metal ion concentration in nonelectrolytic plating liquid from an absorbance E.

[0004] The power applied to the light source 2 was controlled by the light source electric power regulator 5 so that the photosensor 4 arranged near the light source 2 always detected the amount L0 of floodlighting and this amount L0 of floodlighting became fixed conventionally, as shown in drawing 3 . Thus, since the amount L0 of floodlighting is controlled uniformly, CPU7 can calculate permeability t only based on the output of the photosensor 3 amplified by pre amplifier 6. However, since plating liquid concentration becomes high, and the absolute value of the amount L1 of transmitted lights will become small if permeability falls, the output of photosensor 3 becomes minute. Therefore, the problem of becoming large as compared with the case where plating liquid concentration is low had the error of the value of the absorbance E computed as $E=\log (1/t)$.

[0005] [Problem(s) to be Solved by the Invention] This invention solves the above-mentioned conventional trouble, and also when plating liquid concentration becomes high and permeability falls, it is made in order to offer the metal ion density measurement approach of the nonelectrolytic plating liquid which measurement of metal ion concentration can improve precision like the case where plating liquid concentration is low.

[0006] [Means for Solving the Problem] In measuring the metal ion concentration of nonelectrolytic plating liquid with an absorptiometry, this invention made in order to

solve the above-mentioned technical problem is characterized by heightening the output of the light source, when permeability falls, and measuring by making the amount of floodlighting increase. The gestalt of desirable operation of this invention is explained below.

[0007] [Embodiment of the Invention]

[1st operation gestalt] Drawing 1 is drawing showing the 1st operation gestalt of this invention, and the photosensor with which the flow cell to which, as for 1, nonelectrolytic plating liquid is led, and 2 receive the light sources, such as LED, like the conventional example, and 3 receives the transmitted light, the photosensor with which 4 has been arranged near the light source 2, and 5 are light source electric power regulators. The output of photosensor 3 is inputted into CPU7 after it was inputted into CPU7 after being amplified by pre amplifier 6, and the output of photosensor 4 is also amplified by pre amplifier 8. CPU7 is t=L1 / L0 from the amount L0 of floodlighting, and the amount L1 of transmitted lights. Permeability t is calculated by the formula.

[0008] the increase of power which supplies a signal to the light source electric power regulator 5 from CPU7 at delivery and the light source 2 when said permeability t which CPU7 calculated in this invention falls, although permeability will fall and the amount L1 of transmitted lights will decrease if plating liquid concentration becomes high as carried out -- amount Lof floodlighting 0 is made to increase For this reason, since the absolute value of the amount L1 of transmitted lights increases also when permeability falls, the error of an absorbance E does not become large like before as compared with the case where plating liquid concentration is low.

[0009] [2nd operation gestalt] Drawing 2 is drawing showing the 2nd operation gestalt of this invention. With this operation gestalt, the output A of the photosensor 3 which receives the transmitted light of the flow cell 1 to which nonelectrolytic plating liquid is led, and the output B of the photosensor 4 which detects the amount L0 of floodlighting from the light source 2 are compared by the comparator 9, and choose a signal with the larger high order selecting switch 10. And a control signal is sent to the light source electric power regulator 5 so that the selected signal may be kept constant, and the output of the light source 2 is controlled.

[0010] With this operation gestalt, in below the highest metal ion concentration of the stationary at the time of real use, it designs so that the output A of photosensor 3 may become large and may consist of an output B of photosensor 4 near the maximum output. In below the highest metal ion of the stationary at the time of real use, like the 1st operation gestalt, since the light source electric power regulator 5 controls the amount of floodlighting of the light source 2 so that the output A of the photosensor 3 which receives the transmitted light becomes fixed, the measurement error of an absorbance can be made small. Moreover, if metal ion concentration turns into more than the maximum density of a stationary and the output B of photosensor 4 becomes large from the output A of photosensor 3, the high order selecting switch 10 will choose an output B, and the output of the light source 2 is controlled so that the output B of the photosensor 4 which detects the amount L0 of floodlighting from the light source 2 becomes fixed. By this, since the output B of photosensor 4 is not saturated, it can utilize the dynamic range of a measuring circuit effectively, and it can raise the accuracy of measurement at the time of real use.

[0011] [Effect of the Invention] Since the output of the light source is heightened and it

was made to measure by making the amount of floodlighting increase when the permeability of nonelectrolytic plating liquid fell according to this invention as explained above, the fall of the accuracy of measurement accompanying reduction of the amount of transmitted lights can be prevented, and there is an advantage which can measure metal ion concentration in the precision stabilized irrespective of concentration change of nonelectrolytic plating liquid.

## PRIOR ART

[Description of the Prior Art] The metal ion in plating liquid deposits as a metal on a work-piece front face by the catalytic reduction reaction of a work-piece metal, and along with it, metal ion concentration, reducing-agent concentration, pH, etc. fall gradually, and go by nonelectrolytic plating, such as non-electrolyzed nickel plating. Therefore, plating liquid is sampled, metal ion concentration is measured with an absorptiometry, and plating liquid management maintained at the value which was always able to define the amount of metal ions in plating liquid etc. is performed.

[0003] The metal ion density measurement by this absorptiometry leads nonelectrolytic plating liquid to the interior of a flow cell 1, as shown in drawing 3 , and it is performed by the approach of measuring the quantity of light which applied light from the light source 2 and was penetrated with photosensor 3. When the amount of floodlighting from the light source 2 is set to L0 and the amount of transmitted lights measured by photosensor 3 is set to L1, it is $t=L1 / L0$. It is called permeability and $E=\log(1/t)$ is called absorbance. In this case, since an absorbance E is generally in direct proportion to metal ion concentration, it can ask for the metal ion concentration in nonelectrolytic plating liquid from an absorbance E.

[0004] The power applied to the light source 2 was controlled by the light source electric power regulator 5 so that the photosensor 4 arranged near the light source 2 always detected the amount L0 of floodlighting and this amount L0 of floodlighting became fixed conventionally, as shown in drawing 3 . Thus, since the amount L0 of floodlighting is controlled uniformly, CPU7 can calculate permeability t only based on the output of the photosensor 3 amplified by pre amplifier 6. However, since plating liquid concentration becomes high, and the absolute value of the amount L1 of transmitted lights will become small if permeability falls, the output of photosensor 3 becomes minute. Therefore, the problem of becoming large as compared with the case where plating liquid concentration is low had the error of the value of the absorbance E computed as $E=\log(1/t)$.

## EFFECT OF THE INVENTION

[Effect of the Invention] Since the output of the light source is heightened and it was made to measure by making the amount of floodlighting increase when the permeability of nonelectrolytic plating liquid fell according to this invention as explained above, the fall of the accuracy of measurement accompanying reduction of the amount of transmitted lights can be prevented, and there is an advantage which can measure metal ion concentration in the precision stabilized irrespective of concentration change of nonelectrolytic plating liquid

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned conventional trouble, and also when plating liquid concentration becomes high and permeability falls, it is made in order to offer the metal ion density measurement approach of the nonelectrolytic plating liquid which measurement of metal ion concentration can improve precision like the case where plating liquid concentration is low.

[0006] MEANS

[Means for Solving the Problem] In measuring the metal ion concentration of nonelectrolytic plating liquid with an absorptiometry, this invention made in order to solve the above-mentioned technical problem is characterized by heightening the output of the light source, when permeability falls, and measuring by making the amount of floodlighting increase. The gestalt of desirable operation of this invention is explained below.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the block diagram showing the 1st operation gestalt.
[Drawing 2] It is the block diagram showing the 2nd operation gestalt.
[Drawing 3] It is the block diagram showing a conventional method.
[Description of Notations]
1 Flow Cell to which Nonelectrolytic Plating Liquid is Led
2 Light Source
3 Photosensor Which Receives Transmitted Light
4 Photosensor Which Detects the Amount L0 of Floodlighting
5 Light Source Electric Power Regulator
6 Pre Amplifier
7 CPU
8 Pre Amplifier
9 Comparator
10 High Order Selecting Switch

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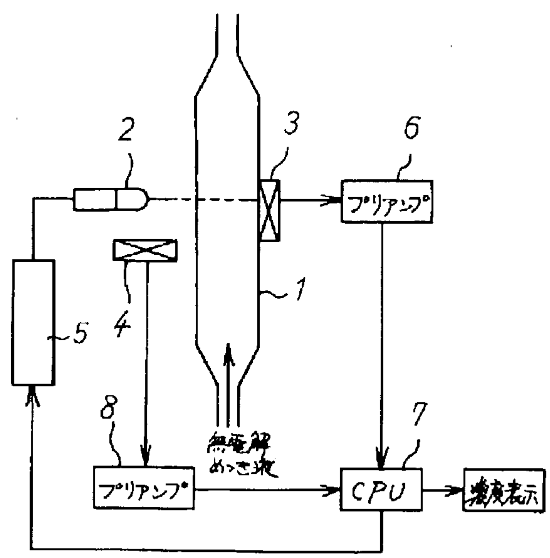
(54)【発明の名称】　無電解めっき液の金属イオン濃度測定方法

(57)【要約】

【課題】　無電解めっき液の濃度変化にかかわらず安定した精度で金属イオン濃度を測定できる吸光光度法による金属イオン濃度測定方法を提供する。

【解決手段】　無電解めっき液の金属イオン濃度を吸光光度法により測定するに当たり、無電解めっき液の濃度が高くなり透過率が低下したときでも、透過光を受光するフォトセンサー３の出力Ａが大幅に減少しないように光源電力制御器５によって光源２に供給する電力を増やし、投光量を増加させて測定を行う。



1

【特許請求の範囲】

【請求項1】　無電解めっき液の金属イオン濃度を吸光光度法により測定するに当たり、透過率が低下したときに光源の出力を高め、投光量を増加させて測定を行うことを特徴とする無電解めっき液の金属イオン濃度測定方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、吸光光度法による無電解めっき液の金属イオン濃度測定方法に関するものである。

【0002】

【従来の技術】無電解ニッケルめっき等の無電解めっきでは、めっき液中の金属イオンがワーク金属の触媒還元反応によりワーク表面に金属として析出し、それにつれて金属イオン濃度、還元剤濃度、pH等が徐々に低下して行く。そのため、めっき液をサンプリングして吸光光度法により金属イオン濃度を測定し、めっき液中の金属イオン量等を常に定められた値に保つめっき液管理が行われている。

【0003】この吸光光度法による金属イオン濃度測定は、図3に示すように無電解めっき液をフローセル1の内部に導き、光源2から光を当ててフォトセンサー3により透過した光量を測定する方法で行われている。光源2からの投光量を$L_0$とし、フォトセンサー3により測定された透過光量を$L_1$としたとき、$t=L_1/L_0$ を透過率といい、$E=\log(1/t)$を吸光度という。この場合一般に吸光度Eは金属イオン濃度に正比例するので、吸光度Eから無電解めっき液中の金属イオン濃度を求めることができる。

【0004】従来は図3に示すように、光源2の近傍に配置されたフォトセンサー4により投光量$L_0$を常時検出してこの投光量$L_0$が一定となるように光源電力制御器5で光源2に加える電力を制御していた。このように投光量$L_0$を一定に制御しているため、CPU7はプリアンプ6で増幅されたフォトセンサー3の出力のみに基づいて透過率tを演算することができる。ところがめっき液濃度が高くなり透過率が低下すると透過光量$L_1$の絶対値が小さくなるため、フォトセンサー3の出力は微小となる。従って、$E=\log(1/t)$として算出される吸光度Eの値の誤差は、めっき液濃度が低い場合に比較して大きくなるという問題があった。

【0005】

【発明が解決しようとする課題】本発明は上記した従来の問題点を解決し、めっき液濃度が高くなり透過率が低下した場合にも、めっき液濃度が低い場合と同様に精度良く金属イオン濃度の測定ができる無電解めっき液の金属イオン濃度測定方法を提供するためになされたものである。

【0006】

2

【課題を解決するための手段】上記の課題を解決するためになされた本発明は、無電解めっき液の金属イオン濃度を吸光光度法により測定するに当たり、透過率が低下したときに光源の出力を高め、投光量を増加させて測定を行うことを特徴とするものである。以下に本発明の好ましい実施の形態を説明する。

【0007】

【発明の実施の形態】

〔第1の実施形態〕図1は本発明の第1の実施形態を示す図であり、従来例と同様、1は無電解めっき液が導かれるフローセル、2はLED等の光源、3は透過光を受光するフォトセンサー、4は光源2の近傍に配置されたフォトセンサー、5は光源電力制御器である。フォトセンサー3の出力はプリアンプ6で増幅されたうえでCPU7に入力され、またフォトセンサー4の出力もプリアンプ8で増幅されたうえでCPU7に入力される。CPU7は投光量$L_0$と透過光量$L_1$から$t=L_1/L_0$ の式により透過率tを演算する。

【0008】前記したようにめっき液濃度が高くなると透過率が低下し透過光量$L_1$が減少するが、本発明においてはCPU7が演算した透過率tが低下したとき、CPU7から光源電力制御器5に信号を送り、光源2に供給する電力を増し投光量$L_0$を増加させる。このため、透過率が低下したときにも透過光量$L_1$の絶対値が増加するので、従来のように吸光度Eの誤差がめっき液濃度が低い場合に比較して大きくなることはない。

【0009】〔第2の実施形態〕図2は本発明の第2の実施形態を示す図である。この実施形態では、無電解めっき液が導かれるフローセル1の透過光を受光するフォトセンサー3の出力Aと、光源2からの投光量$L_0$を検出するフォトセンサー4の出力Bとが比較器9で比較され、高位選択スイッチ10が大きい方の信号を選択する。そして選択された信号が一定に保たれるように光源電力制御器5に制御信号が送られ、光源2の出力を制御する。

【0010】この実施形態では、実使用時の定常の最高金属イオン濃度以下の場合、フォトセンサー3の出力Aがフォトセンサー4の出力Bより大きくなり、最大出力近くになるように設計しておく。実使用時の定常の最高金属イオン以下の場合には、第1の実施形態と同様に、透過光を受光するフォトセンサー3の出力Aが一定になるように光源電力制御器5が光源2の投光量を制御するので、吸光度の測定誤差を小さくすることができる。また金属イオン濃度が定常の最高濃度以上となり、フォトセンサー3の出力Aよりフォトセンサー4の出力Bが大きくなると高位選択スイッチ10が出力Bを選択し、光源2からの投光量$L_0$を検出するフォトセンサー4の出力Bが一定になるように光源2の出力が制御される。これによってフォトセンサー4の出力Bは飽和しないので測定回路のダイナミックレンジを有効に活用することがで

き、実使用時の測定精度を向上させることができる。

【００１１】

【発明の効果】以上に説明したように、本発明によれば無電解めっき液の透過率が低下したときに光源の出力を高め、投光量を増加させて測定を行うようにしたので、透過光量の減少に伴う測定精度の低下が防止でき、無電解めっき液の濃度変化にかかわらず安定した精度で金属イオン濃度を測定できる利点がある。

【図面の簡単な説明】

【図１】第１の実施形態を示すブロック図である。

【図２】第２の実施形態を示すブロック図である。

【図３】従来法を示すブロック図である。

【符号の説明】

１　無電解めっき液が導かれるフローセル

２　光源

３　透過光を受光するフォトセンサー

４　投光量$L_0$を検出するフォトセンサー

５　光源電力制御器

６　プリアンプ

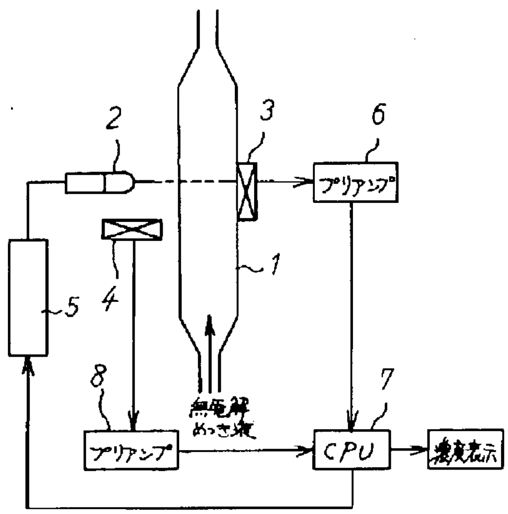
７　ＣＰＵ

８　プリアンプ

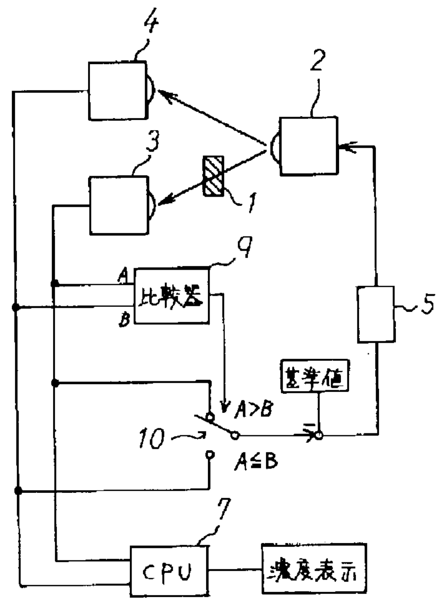
９　比較器

１０　高位選択スイッチ

【図１】




【図２】



【図3】